TOPICS

The Kinetic Theory of Gases

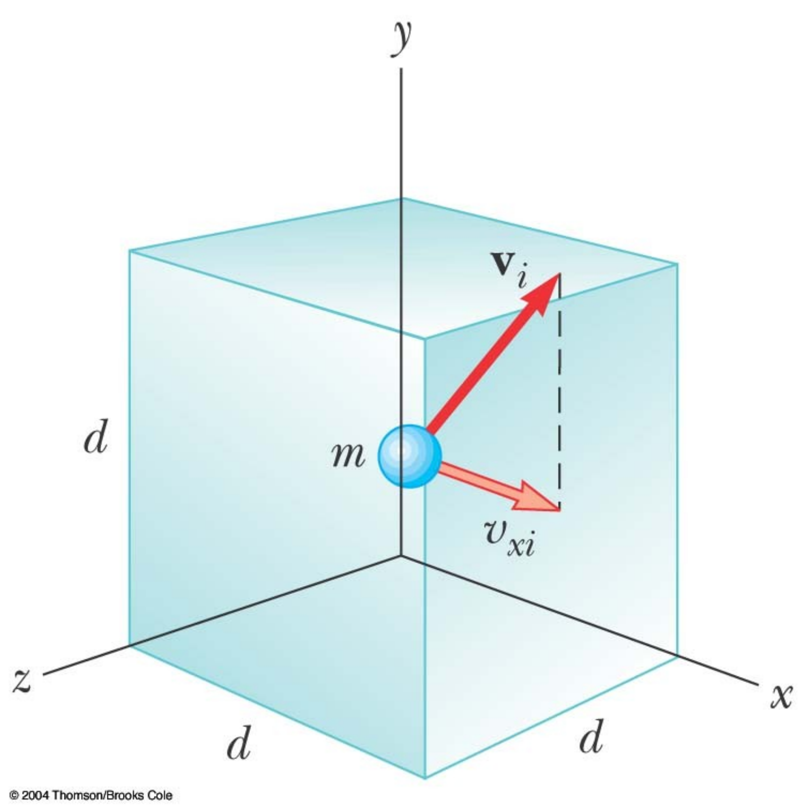
Equipartion of Energy

Molar Specific Heat

Mean Free Path

Pressure and Kinetic Energy

- Assume a container is a cube
  - Edges are length *d*
- Look at the motion of the molecule in terms of its velocity components
- Look at its momentum and the average force



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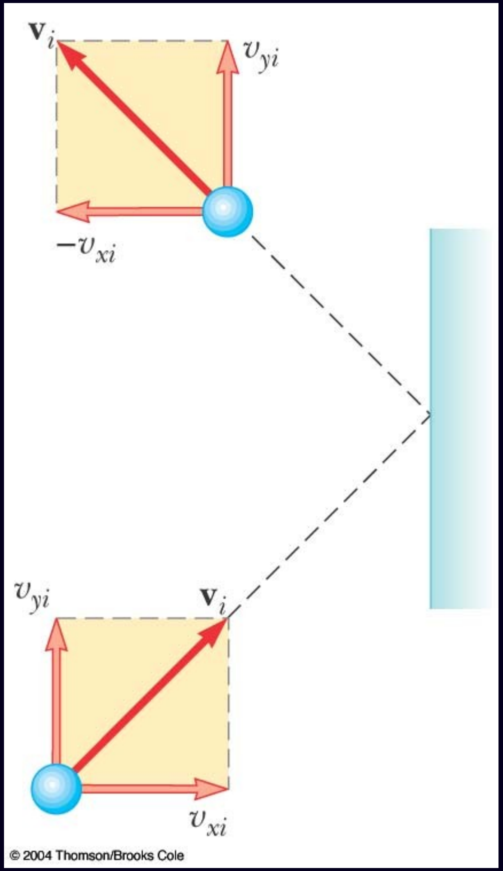
Pressure and Kinetic Energy,
Continued

- Assume perfectly elastic collisions with the walls of the container
- The relationship between the pressure and the molecular kinetic energy comes from momentum and Newton's Laws



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Calculating the pressure

- The change in momentum of the molecule shown is $\Delta p_x = 2p_x = 2mv_x$.
- The force on the wall, averaged over a complete trip, is $F_x = \Delta p_x / \Delta t$,
- Where $\Delta t = 2d/v_x$.
- Putting this together, we have
  - $F_x = mv_x^2/d$.

Continuing…

- Now this was for just one molecule. For the total force, we add the above expression for each molecule:
- $F_{x,tot} = (m\Sigma v_{x,i}^2)/d.$
- The summed quantity is related to the average of the quantity v_x^2:
- $(v_x^2)_{ave} = \Sigma v_{x,i}^2/N.$

Continued...

- We also know that the average of v_x^2 is the same as avg. of v_y^2 and v_z^2, since the velocities are random. Therefore,
- $(v_x^2)_{ave} = 1/3(v^2)_{ave}$
- Putting the last two relations into the formula for the force, we get
- $F_{x,tot} = Nm\,(v^2)_{ave}/(3d).$

Conclusions

- This is the total force on one side of the box. The pressure is this force divided by the area of the side, d^2. Since d^3 = the volume V, we get:
- $P = Nm\,(v^2)_{ave}/3V$.
- The average kinetic energy of a molecule is $K_{ave} = \frac{1}{2}\,m\,(v^2)_{ave}$

Still concluding

- So we can rewrite the pressure as
- $P = 2/3\ (N/V)\ K_{ave.}$
- Rearranging:
- $PV = 2/3\ N\ K_{ave}$.
- Now we already know that $PV = nRT$
- So $nRT = 2/3\ N\ K_{ave}$.

continued

- Therefore, we can see that K and T are proportional:
- $K_{ave} = 3/2\ nRT/N$ = avg. K per molecule.
- Now $N = nN_A$, so
- $K_{ave} = 3/2\ (R/N_A)T = 3/2\ k_BT$., therefore
- $K_{ave} = 3/2\ k_BT$.

Equipartition of Energy

- Note that $(\frac{1}{2} m v_x^2)_{ave} = \frac{1}{2} k_B T$, and similarly for y and z. More generally,
- The average energy per molecule for each degree of freedom is $\frac{1}{2} k_B T$.
- Degrees of freedom include translation, rotation, and vibration.

RMS velocity

- Starting with $(\frac{1}{2} mv^2)_{ave} = 3/2\ k_B T$,
- We solve for v^2 to find
- $v^2_{ave} = 3\ k_B T/m = 3RT/M$,
- where M = molar mass. Take sqrt:
- v_{rms} = sqrt $(3RT/M)$.

Some Example v_{rms} Values

At a given temperature, lighter molecules move faster, on the average, than heavier molecules

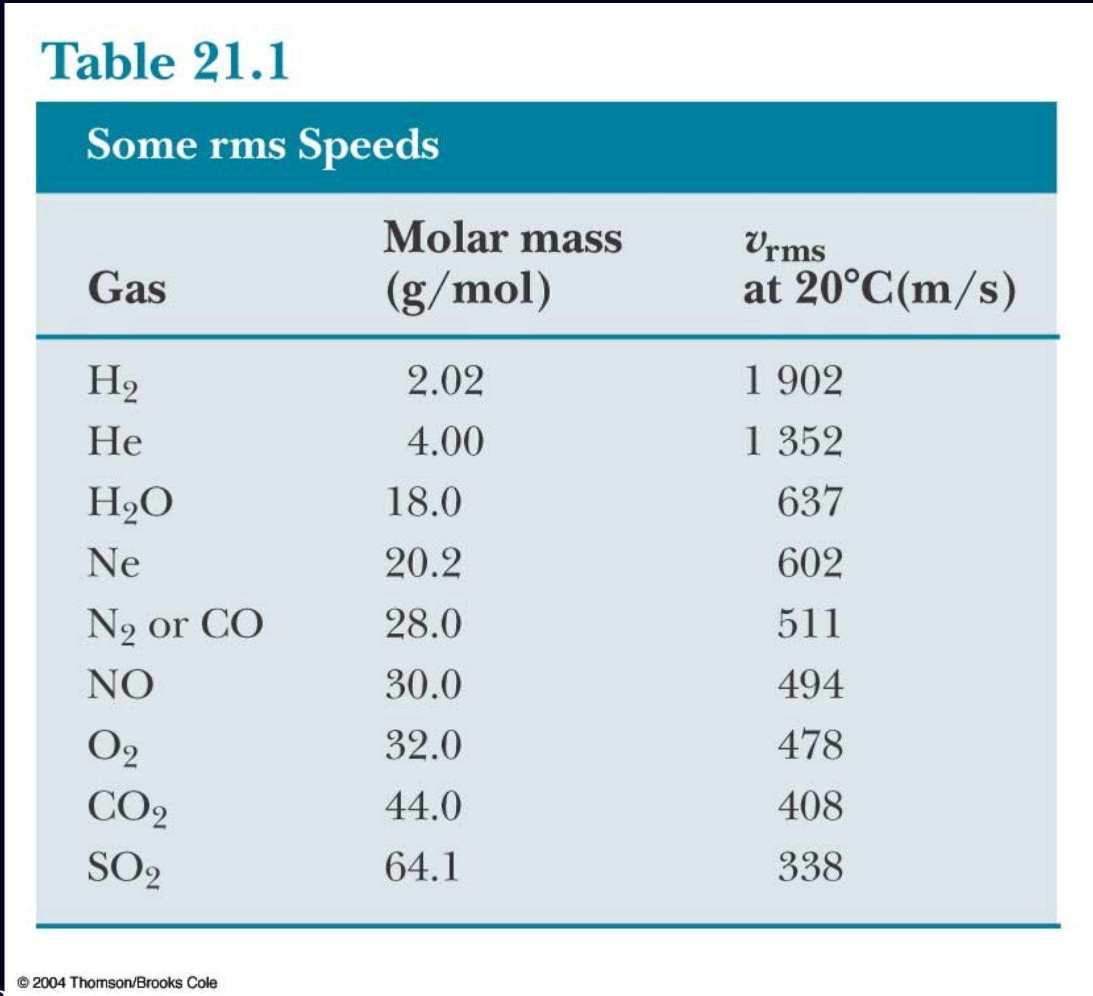

Table 21.1

Some rms Speeds

Gas	Molar mass (g/mol)	v_{rms} at 20°C(m/s)
H_2	2.02	1 902
He	4.00	1 352
H_2O	18.0	637
Ne	20.2	602
N_2 or CO	28.0	511
NO	30.0	494
O_2	32.0	478
CO_2	44.0	408
SO_2	64.1	338

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Total Kinetic Energy

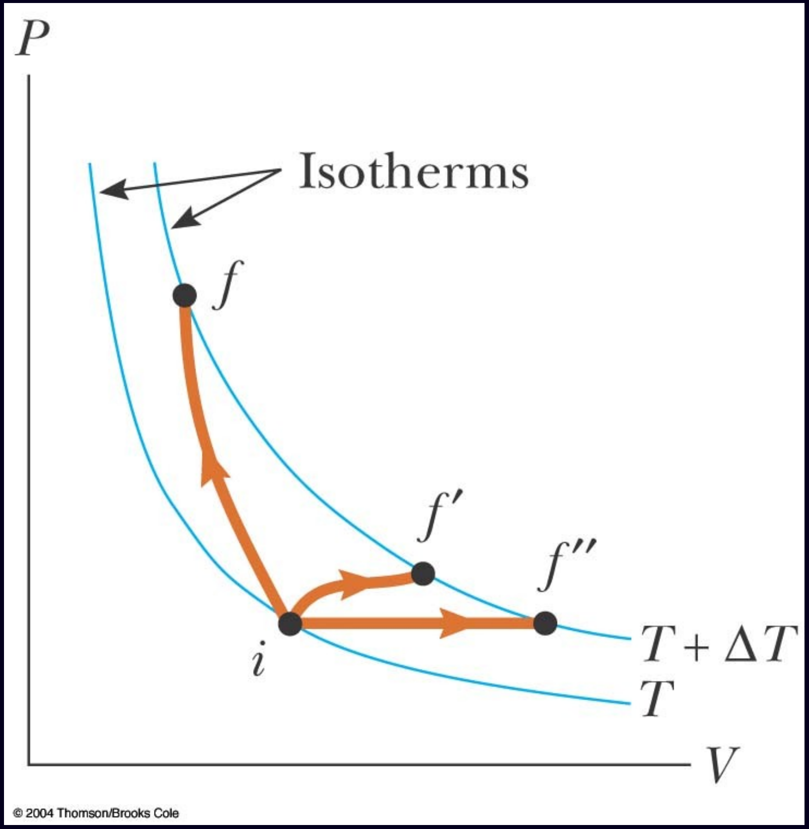
- The total kinetic energy is just *N* times the kinetic energy of each molecule

$$K_{\text{tot trans}} = N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{3}{2}Nk_B T = \frac{3}{2}nRT$$

- If we have a gas with only translational energy, this is the internal energy of the gas
- This tells us that the internal energy of an ideal gas depends only on the temperature

Molar Specific Heat

- Several processes can change the temperature of an ideal gas
- Since ΔT is the same for each process, ΔE_{int} is also the same
- The heat is different for the different paths
- The heat associated with a particular change in temperature is **not** unique



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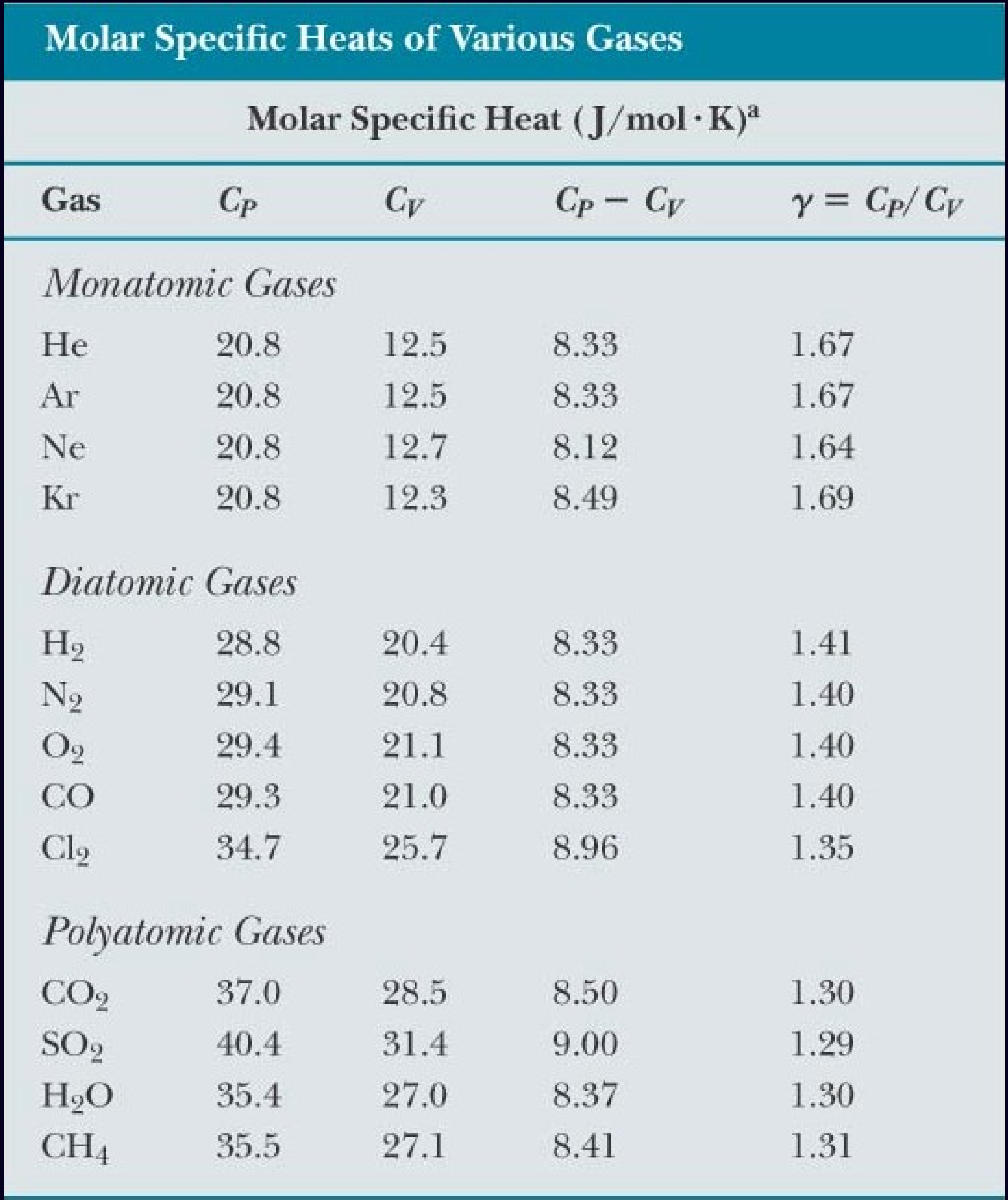
Molar Specific Heat, continued

- We define specific heats for two processes that frequently occur:
  - Changes with constant pressure
  - Changes with constant volume
- Using the number of moles, *n*, we can define molar specific heats for these processes

Molar Specific Heat, Continued

- Molar specific heats:
  - $Q = nC_V \Delta T$ for constant-volume processes
  - $Q = nC_P \Delta T$ for constant-pressure processes
- *Q* (constant pressure) must account for both the increase in internal energy and the transfer of energy out of the system by work
- $Q_{\text{constant } P} > Q_{\text{constant } V}$ for given values of *n* and ΔT

Sample Values of Molar Specific Heats

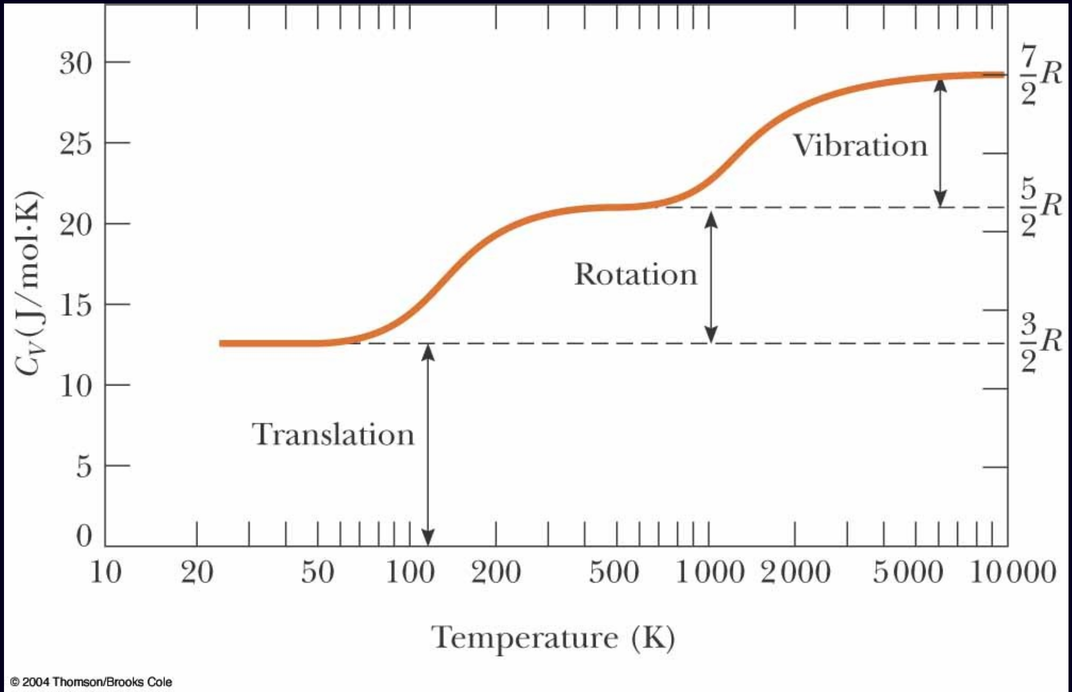


Molar Specific Heats of Various Gases

Gas	Molar Specific Heat (J/mol·K)[a] C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

Agreement with Experiment

- Molar specific heat is a function of temperature
- At low temperatures, a diatomic gas acts like a monatomic gas
  - $C_V = 3/2\ R$



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Pressure and Kinetic Energy, 3

- The relationship is

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right)$$

- This tells us that pressure is proportional to the number of molecules per unit volume (N/V) and to the average translational kinetic energy of the molecules

Molecular Model of an Ideal Gas

- The model shows that the pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas with the walls
- It is consistent with the macroscopic description developed earlier

Ideal Gas Assumptions

- The number of molecules in the gas is large, and the average separation between the molecules is large compared with their dimensions
    - The molecules occupy a negligible volume within the container
    - This is consistent with the macroscopic model where we assumed the molecules were point-like

Ideal Gas Assumptions, 2

- The molecules obey Newton’s laws of motion, but as a whole they move randomly
  - Any molecule can move in any direction with any speed
  - At any given moment, a certain percentage of molecules move at high speeds
  - Also, a certain percentage move at low speeds

Ideal Gas Assumptions, 3

- The molecules interact only by short-range forces during elastic collisions
  - This is consistent with the macroscopic model, in which the molecules exert no long-range forces on each other
- The molecules make elastic collisions with the walls
- The gas under consideration is a pure substance
  - All molecules are identical

Ideal Gas Notes

- An ideal gas is often pictured as consisting of single atoms
- However, the behavior of molecular gases approximate that of ideal gases quite well
  - Molecular rotations and vibrations have no effect, on average, on the motions considered

Pressure and Kinetic Energy, final

- This equation also relates the macroscopic quantity of pressure with a microscopic quantity of the average value of the square of the molecular speed
- One way to increase the pressure is to increase the number of molecules per unit volume
- The pressure can also be increased by increasing the speed (kinetic energy) of the molecules

Molecular Interpretation of Temperature

- We can take the pressure as it relates to the kinetic energy and compare it to the pressure from the equation of state for an ide

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right) = Nk_B T$$

- Therefore, the temperature is a direct measure of the average molecular kinetic energy

Molecular Interpretation of Temperature, cont

- Simplifying the equation relating temperature and kinetic energy gives

$$\frac{1}{2} m\overline{v^2} = \frac{3}{2} k_B T$$

- This can be applied to each direction,

$$\frac{1}{2} m\overline{v_x^2} = \frac{1}{2} k_B T$$

with similar expressions for v_y and v_z

A Microscopic Description of Temperature, final

- Each translational degree of freedom contributes an equal amount to the energy of the gas
    - In general, a degree of freedom refers to an independent means by which a molecule can possess energy
- A generalization of this result is called the **theorem of equipartition of energy**

Theorem of Equipartition of Energy

- Each degree of freedom contributes ½$k_B T$ to the energy of a system, where possible degrees of freedom in addition to those associated with translation arise from rotation and vibration of molecules

Root Mean Square Speed

- The root mean square (rms) speed is the square root of the average of the squares of the speeds
  - Square, average, take the square root
- Solving for v_{rms} we find

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

- M is the molar mass and $M = mN_A$

Ideal Monatomic Gas

- A monatomic gas contains one atom per molecule
- When energy is added to a monatomic gas in a container with a fixed volume, all of the energy goes into increasing the translational kinetic energy of the gas
  - There is no other way to store energy in such a gas

Ideal Monatomic Gas, cont

- Therefore, $\Delta E_{\text{int}} = 3/2\ nRT$
  - ΔE is a function of T only
- In general, the internal energy of an ideal gas is a function of T only
  - The exact relationship depends on the type of gas
- At constant volume, $Q = \Delta E_{\text{int}} = nC_V\ \Delta T$
  - This applies to all ideal gases, not just monatomic ones

Monatomic Gases, final

- Solving for C_V gives $C_V = 3/2\ R = 12.5\ \text{J/mol} \cdot \text{K}$
  - For all monatomic gases
  - This is in good agreement with experimental results for monatomic gases
- In a constant-pressure process, $\Delta E_{\text{int}} = Q + W$ and $C_P - C_V = R$
  - This also applies to any ideal gas
  - $C_p = 5/2\ R = 20.8\ \text{J/mol} \cdot \text{K}$

Ratio of Molar Specific Heats

- We can also define

$$\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = 1.67$$

- Theoretical values of C_V, C_P, and γ are in excellent agreement for monatomic gases
- But they are in serious disagreement with the values for more complex molecules
  - Not surprising since the analysis was for monatomic gases

Molar Specific Heats of Other Materials

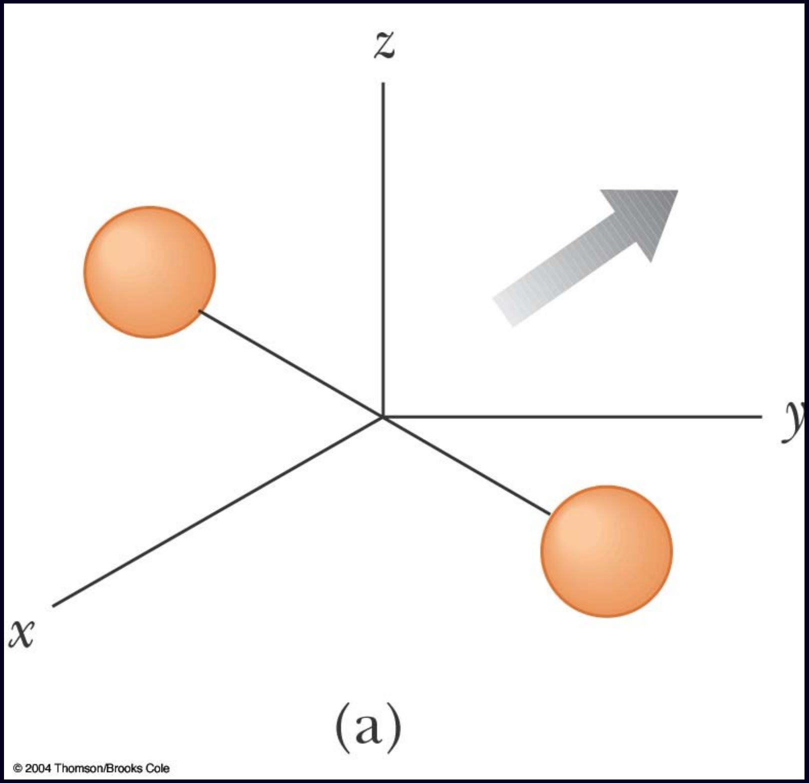
- The internal energy of more complex gases must include contributions from the rotational and vibrational motions of the molecules
- *In the cases of solids and liquids heated at constant pressure, very little work is done since the thermal expansion is small and* C_P *and* C_V *are approximately equal*

Adiabatic Processes for an Ideal Gas

- Assume an ideal gas is in an equilibrium state and so $PV = nRT$ is valid
- The pressure and volume of an ideal gas at any time during an adiabatic process are related by $PV^{\gamma} = \text{constant}$
- $\gamma = C_P / C_V$ is assumed to be constant during the process
- All three variables in the ideal gas law (P, V, T) can change during an adiabatic process

Equipartition of Energy

- With complex molecules, other contributions to internal energy must be taken into account
- One possible energy is the translational motion of the center of mass



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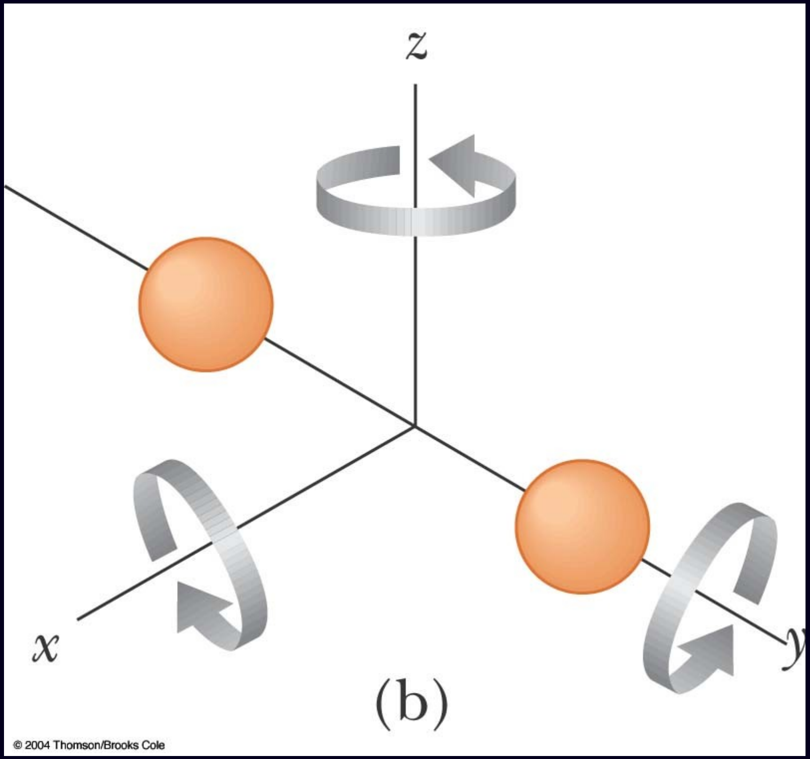
Equipartition of Energy, cont..

- Rotational motion about the various axes also contributes
  - We can neglect the rotation around the *y* axis since it is negligible compared to the *x* and *z* axes



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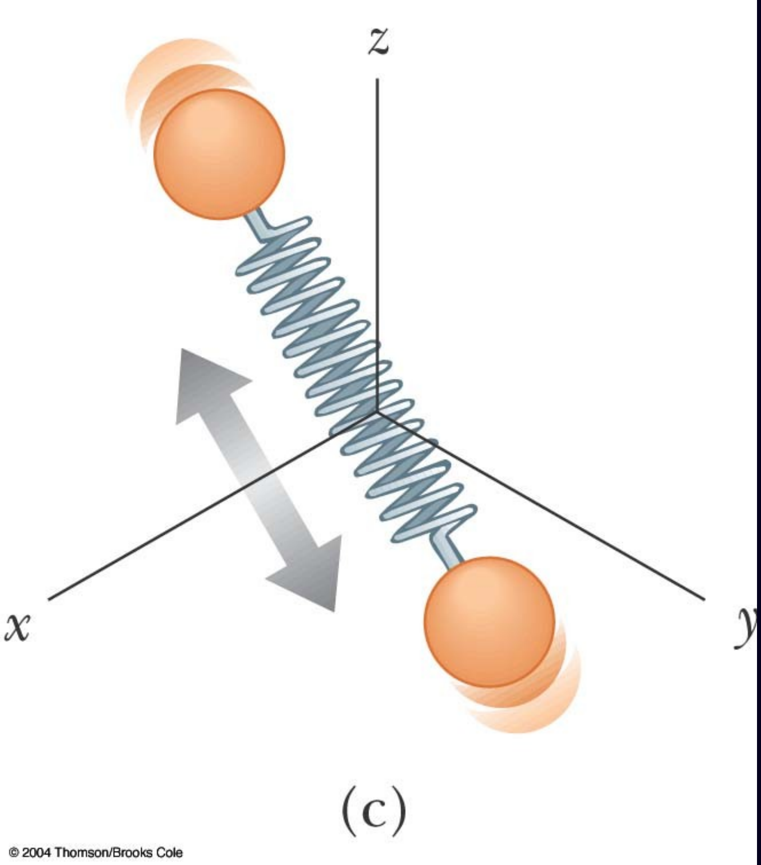
Equipartition of Energy, cont…

- The molecule can also vibrate
- There is kinetic energy and potential energy associated with the vibrations



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Equipartition of Energy, cont…

- The translational motion adds three degrees of freedom
- The rotational motion adds two degrees of freedom
- The vibrational motion adds two more degrees of freedom
- Therefore, $E_{\text{int}} = 7/2\ nRT$ and $C_V = 7/2\ R$
- This is inconsistent with experimental results

Agreement with Experiment, cont…

- At about room temperature, the value increases to $C_V = 5/2\ R$
    - This is consistent with adding rotational energy but not vibrational energy
- At high temperatures, the value increases to $C_V = 7/2\ \mathrm{R}$
    - This includes vibrational energy as well as rotational and translational

Complex Molecules

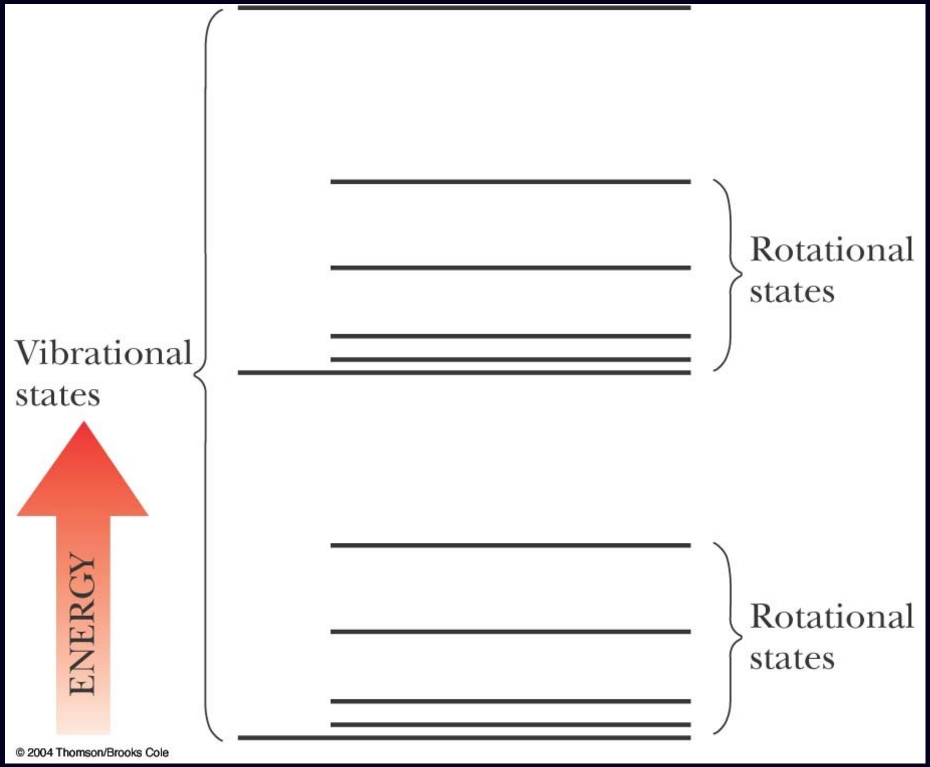
- For molecules with more than two atoms, the vibrations are more complex
- The number of degrees of freedom is larger
- The more degrees of freedom available to a molecule, the more “ways” there are to store energy
  - This results in a higher molar specific heat

Quantization of Energy

- To explain the results of the various molar specific heats, we must use some quantum mechanics
  - Classical mechanics is not sufficient
- In quantum mechanics, the energy is proportional to the frequency of the wave representing the frequency
- The energies of atoms and molecules are quantized

Quantization of Energy, 2

- This energy level diagram shows the rotational and vibrational states of a diatomic molecule
- The lowest allowed state is the **ground state**



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Quantization of Energy, 3

- The vibrational states are separated by larger energy gaps than are rotational states
- At low temperatures, the energy gained during collisions is generally not enough to raise it to the first excited state of either rotation or vibration

Quantization of Energy, 4

- Even though rotation and vibration are classically allowed, they do not occur
- As the temperature increases, the energy of the molecules increases
- In some collisions, the molecules have enough energy to excite to the first excited state
- As the temperature continues to increase, more molecules are in excited states

Quantization of Energy, final

- At about room temperature, rotational energy is contributing fully
- At about 1000 K, vibrational energy levels are reached
- At about 10 000 K, vibration is contributing fully to the internal energy

Molar Specific Heat of Solids

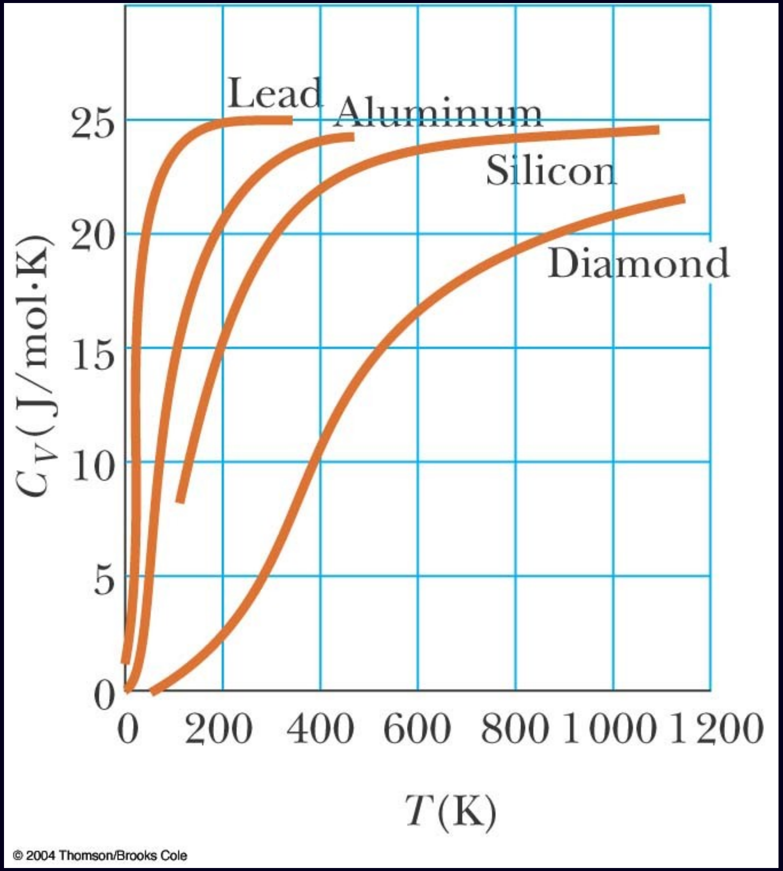
- Molar specific heats in solids also demonstrate a marked temperature dependence
- Solids have molar specific heats that generally decrease in a nonlinear manner with decreasing temperature
- It approaches zero as the temperature approaches absolute zero

DuLong-Petit Law

- At high temperatures, the molar specific heats approach the value of 3R
  - This occurs above 300 K
- The molar specific heat of a solid at high temperature can be explained by the equipartition theorem
  - Each atom of the solid has six degrees of freedom
  - The internal energy is 3 nRT and $C_v = 3\ R$

Molar Specific Heat of Solids, Graph

- As T approaches 0, the molar specific heat approaches 0
- At high temperatures, C_V becomes a constant at ~$3R$



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Boltzmann Distribution Law

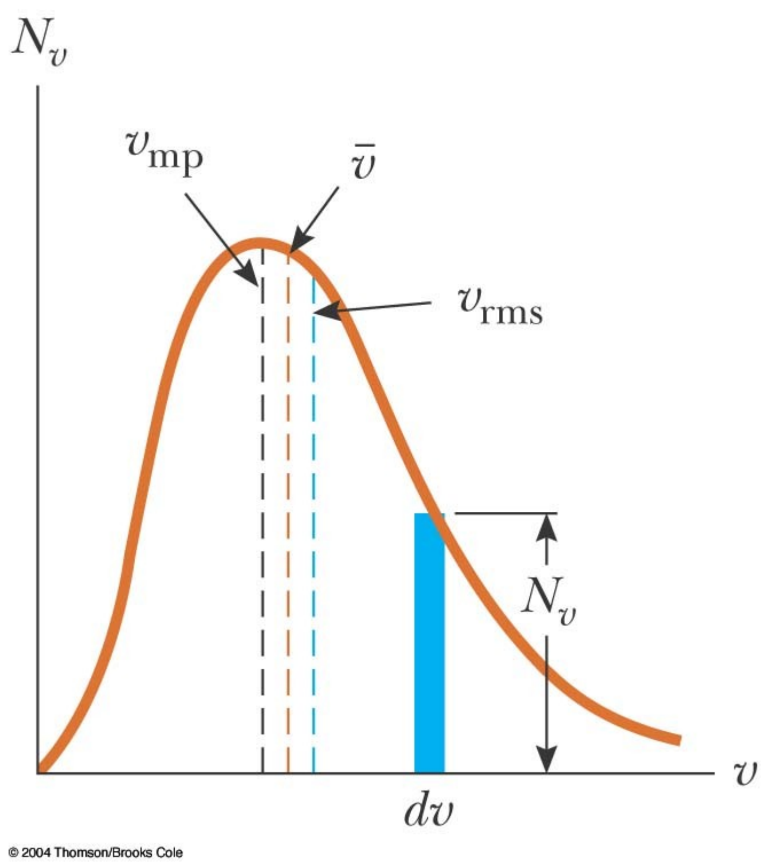
- The motion of molecules is extremely chaotic
- Any individual molecule is colliding with others at an enormous rate
  - Typically at a rate of a billion times per second
- We add the **number density** $n_V(E)$
  - This is called a distribution function
  - It is defined so that $n_V(E)\,dE$ is the number of molecules per unit volume with energy between E and $E + dE$

Number Density and Boltzmann Distribution Law

- From statistical mechanics, the number density is $n_V(E) = n_o e^{-E/k_B T}$
- This equation is known as the Boltzmann distribution law
- It states that the probability of finding the molecule in a particular energy state varies exponentially as the energy divided by $k_B T$

Distribution of Molecular Speeds

- The observed speed distribution of gas molecules in thermal equilibrium is shown at right
- N_V is called the **Maxwell-Boltzmann speed distribution function**



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Distribution Function

- The fundamental expression that describes the distribution of speeds in *N* gas molecules is

$$N_V = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_BT}$$

- m is the mass of a gas molecule, k_B is Boltzmann's constant and T is the absolute temperature

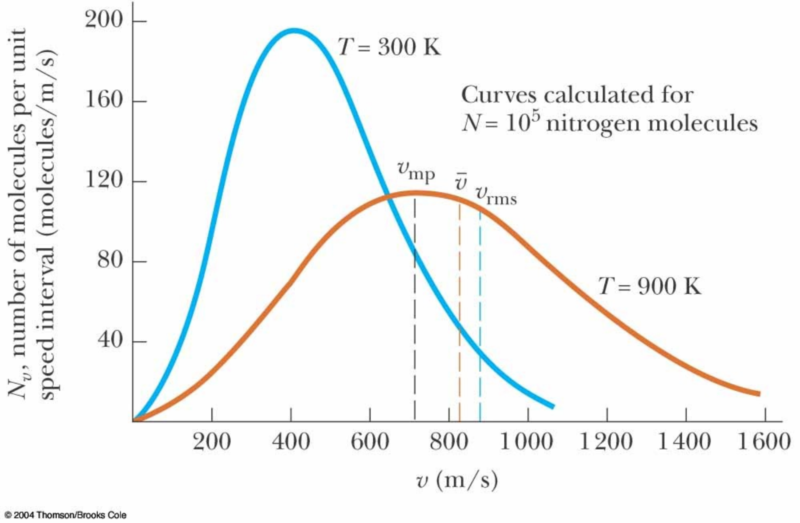
Most Probable Speed

- The average speed is somewhat lower than the rms speed
- The most probable speed, v_{mp} is the speed at which the distribution curve reaches a peak

$$v_{\mathrm{mp}} = \sqrt{\frac{2k_{\mathrm{B}}T}{m}} = 1.41\sqrt{\frac{k_{\mathrm{B}}T}{m}}$$

Speed Distribution

- The peak shifts to the right as *T* increases
  - This shows that the average speed increases with increasing temperature
- The asymmetric shape occurs because the lowest possible speed is 0 and the highest is infinity



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Speed Distribution, final

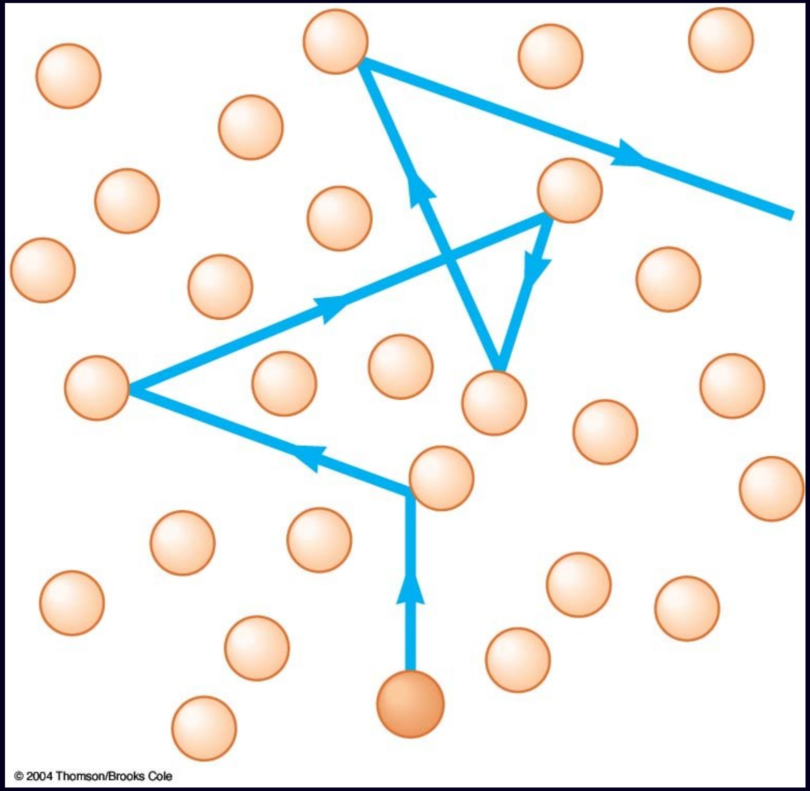
- The distribution of molecular speeds depends both on the mass and on temperature
- The speed distribution for liquids is similar to that of gases

Evaporation

- Some molecules in the liquid are more energetic than others
- Some of the faster moving molecules penetrate the surface and leave the liquid
    - This occurs even before the boiling point is reached
- The molecules that escape are those that have enough energy to overcome the attractive forces of the molecules in the liquid phase
- The molecules left behind have lower kinetic energies
- Therefore, evaporation is a cooling process

Mean Free Path

- A molecule moving through a gas collides with other molecules in a random fashion
- This behavior is sometimes referred to as a *random-walk process*
- The **mean free path** increases as the number of molecules per unit volume decreases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Mean Free Path, cont…

- The molecules move with constant speed along straight lines between collisions
- The average distance between collisions is called the **mean free path**
- The path of an individual molecule is random
  - The motion is not confined to the plane of the paper

Mean Free Path, cont…

- The mean free path is related to the diameter of the molecules and the density of the gas
- We assume that the molecules are spheres of diameter *d*
- No two molecules will collide unless their paths are less than a distance *d* apart as the molecules approach each other

Mean Free Path, final

- The mean free path, ℓ, equals the average distance $v\Delta t$ traveled in a time interval Δt divided by the number of collisions that occur in that time interval:

$$\ell = \frac{\bar{v}\Delta t}{\left(\pi d^2 \bar{v}\Delta t\right) n_V} = \frac{1}{\pi d^2 n_V}$$